

# Acid Resistance of Glass Fibre Composites with Different Layup Sequencing: Part I—Diffusion Studies

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**ABSTRACT:** The effects of sulphuric acid concentration and the sequential layup of glass fibre reinforcements on the diffusion behaviour of glass epoxy composite laminates were studied. In all, composites of six different resin systems viz., general purpose polyester, bis phenol-A polyester, vinyl ester, LY 556 epoxy, and MY 750 epoxy resins, reinforced with different layup sequencing consisting of chopped strand mat (CSM) and woven roving mat (WR) were exposed to sulphuric acid environments of different concentrations.

The results of the study indicated that isophthalic polyester resin exhibited maximum resistance to sulphuric acid while general purpose polyester resin performed relatively inferior. The diffusion phenomenon became anomalous as the concentration of the sulphuric acid increased. Among the layup sequences considered, composite specimens with CSM as the skin layers exhibited higher weight gain than those with WR as the skin layers.

## INTRODUCTION

**T**HE NEED FOR understanding the response of the polymer composites to environmental exposure gave rise to the evaluation of the analytical and experimental methods that predicted property changes within the composite.

Moisture and chemicals (such as acids) are the two most important factors that affect the performance of the composite materials in service. These media can attack the fibre matrix interface, thereby causing substantial loss in the composite strength. This may lead to a catastrophic breakdown of the composite structure, as in the case of FRP battery containers, under prolonged exposure conditions.

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The degradative effects can be directly linked to the levels of moisture and chemicals, diffusing into the composite materials during their exposure to these media. Hence, there is a profound need for realistic assessment of the amount of acid absorbed during the service life of the component and its degradative effects.

Springer et al. [1] made an extensive study of moisture absorption behaviour of polymer composites under various hygrothermal conditions and developed an analytical model for predicting the maximum moisture content and time of saturation. Rao et al. [2] reported the effects of moisture content and fibre volume fraction on Poisson's ratio of glass cloth reinforced epoxy composites. They also modified the Fickian diffusion equations to account for fibre permeability such as that occurring in natural fibre composites. Singh et al. [3] reported on the diffusion of water in epoxy composites with different sequential arrangements of woven roving (WR) and chopped strand mat (CSM) reinforcements on immersion in water at 298 K and 323 K. The CSM laminates showed high diffusivity and equilibrium moisture content than those of the WR laminates. Leitheiser et al. [4] studied the effects of formulation and process variables on polyester resin performance. Patterson [5] studied the effect of gel coats based on isophthalic polyester resins on the flexural strength, toughness, extensibility and chemical resistance of composites in comparison to those with conventional gel coats containing orthophthalic polyester resins. Tr  nt et al. [6] studied the effects of different methods of specimen preparation on the chemical resistance of unsaturated polyester resin laminates and coatings. The results of the absorption studies in corrosive media made by the above authors reflect the resistance of the chosen resin system in terms of property degradation. However, no reports are apparently available on the effect of concentration of the corrosive media and sequential layer of the reinforcement on the diffusion behaviour of polymer composites exposed to acid environments.

Hence, an attempt was made to characterise the diffusion process in various polymer composites as a function of concentration of sulphuric acid as well as the layup sequencing consisting of different forms of glass fibre reinforcement. The validity of a Fickian diffusion model as a function of concentration was also investigated.

## EXPERIMENTAL

### Materials

Two commercially available glass fibres, viz. chopped strand mat (CSM) and Woven Rovings (WR) of E-glass, were chosen for the studies.

The glass forms were available as: 450 g/sq m (CSM) and 350 g/sq m (WR).

The six resin systems chosen were: LY 556 epoxy resin, MY 750 epoxy resin, both of bi-functional (Diglycidyl Ether of Bisphenol A) type, vinyl ester resin, general purpose (orthophthalic) polyester resin, Bisphenol-A resin, Isophthalic polyester resin.

### Laminates

The epoxy resins were cured using 10% triethylene tetramine (TETA) hard-

ener; while the polyesters were promoted with 1% cobalt naphthanate and initiated with 1% methyl ethyl ketone peroxide. The resins were used to impregnate the glass fibre mats using three different stacking sequences, the details of which are given in Figure 1.

All laminates (300 mm  $\times$  300 mm  $\times$  2 mm) were made by using modified hand layup technique developed by Rao et al. [2]. The laminates were post cured at 50°C for two hours and have a fibre volume fraction of around 35%.

### Preparation of Test Specimens and Exposure

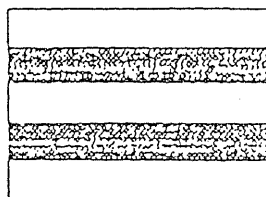
Three specimens of 25 mm  $\times$  25 mm  $\times$  2 mm were cut from each laminate and edge coated with the respective matrix resin system to prevent the edge diffusion effects.

In the first phase of the work, composites of all the six resin systems were fabricated using layup sequence A as in Figure 1, and immersed in sulphuric acid solution of 35% concentration (Sp. Gravity 1.25) and acid absorption levels noted. Based on these studies, the best resin system in terms of superior resistance to acid was chosen. This resin system was then used to study the effects of fabric layup sequences and acid concentration on the diffusion behaviour of composite specimens.

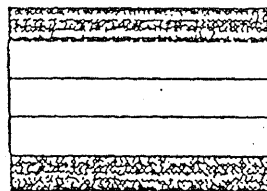
In all the above experiments the test specimens were withdrawn from the acid bath periodically and weighed carefully after wiping them dry. The acid absorption plots (similar to moisture absorption curves) were then generated for each specimen. These results were subsequently used to calculate the maximum percentage weight gain and the diffusion coefficient  $D_c$  of the composite.

#### NOMENCLATURE

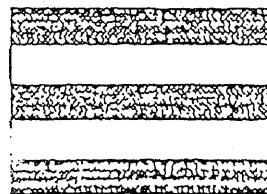
A



B



C



CHOPPED STRAND MAT

WOVEN ROVING MAT

Figure 1. Schematics of different layup sequences used.

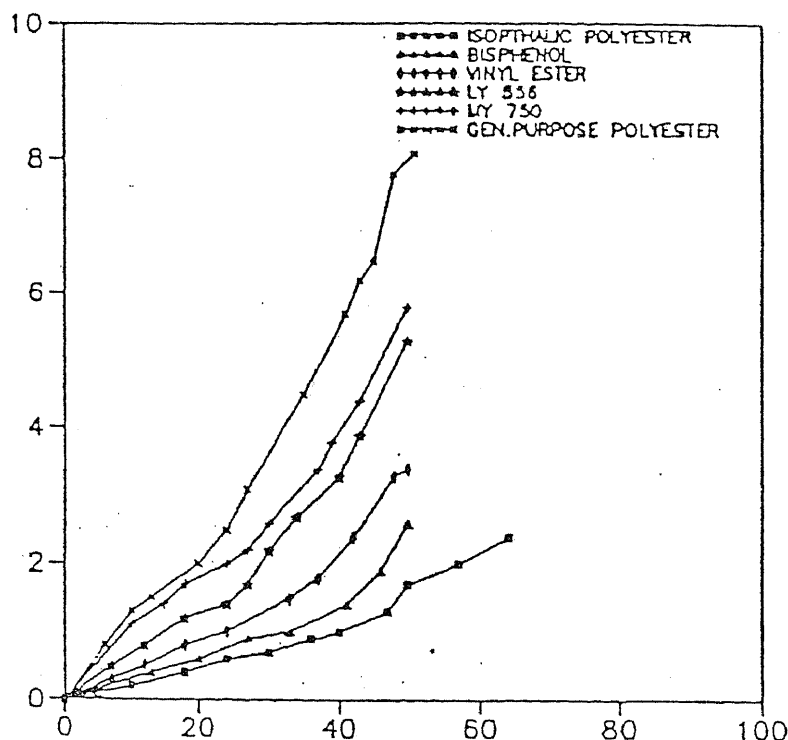


Figure 2. Percentage weight gain values of composites of different resin systems in 35% acid. Title: X-axis: root time in  $(hr^{1/2})$ ; Y-axis: percentage weight gain.

## RESULTS AND DISCUSSIONS

### Identification of Best Resin System

Figure 2 shows the percentage weight gain vs. square root of time for composite specimens of layup sequence A and various resin systems exposed to 35% sulphuric acid (the highest concentration chosen). From the shape and nature of the curves in the figure it is evident that none of the above curves has a shape confirming to the Fickian model, indicating that the diffusion process is evidently non-Fickian at such high acid concentrations. Hence the evaluation of  $D_c$  by the existing Fickian model is impracticable.

Nonetheless, the initial linear slopes of the plots clearly distinguish the relative resistance of various resin systems to the corrosive environment.

Further it is apparent, that isophthalic grade polyester resin exhibits the maximum resistance to sulphuric acid (slope = 0.0317), while the GP Polyester (slope = 0.1383) performs poorly. Studies were therefore continued using isophthalic polyester to study the effects of different acid concentrations and fabric layup sequencing on the diffusion process.

### Effect of Acid Concentration

Composite specimen exhibited anomalous behaviour at high acid concentrations apparently due to the increase in degradation levels at the fibre matrix interface. The net result is the increase in the porosity of the CSM fibres and percent

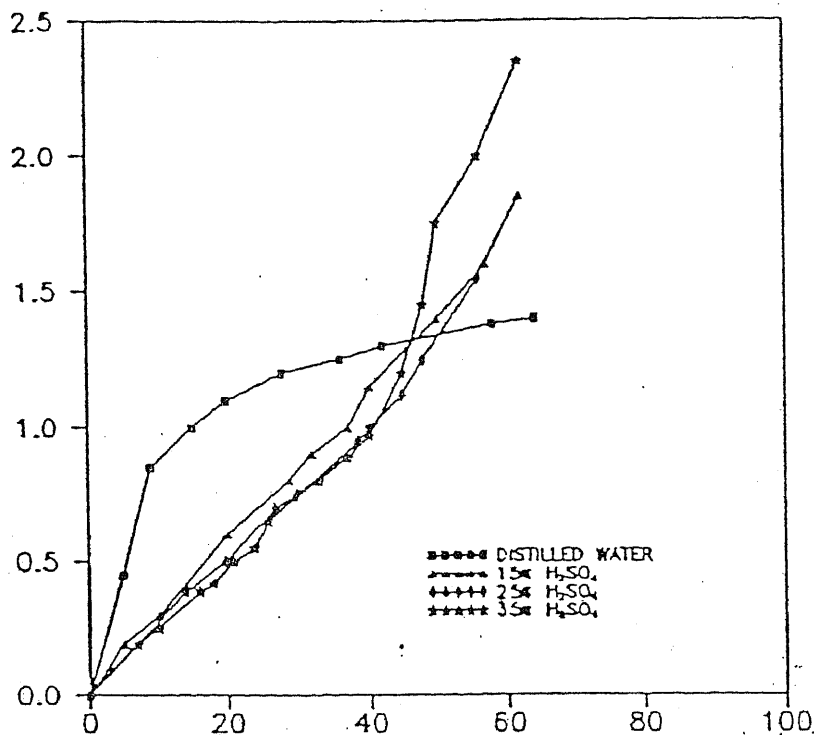


Figure 3. Effect of sulphuric acid concentration on composites of isophthalic polyester resin. Title: X-axis: root-time in  $(hr)^{1/2}$ ; Y-axis: percentage weight gain.

weight gain due to a different mode of absorption, viz, capillary action. In order to study the effect of acid concentration on the diffusion behaviour (and hence on the validity of a Fickian model), Isophthalic Polyester composites of layup sequence A were chosen. The composite specimens were exposed to sulphuric acid of concentrations 0%, 15%, 25% and 35% by weight.

Figure 3 shows the acid absorption curves for different acid concentrations for the isophthalic polyester resin based composites. From the initial linear slopes, it is evident that the diffusion becomes sluggish as the concentration of acid increases.

### FICKIAN BEHAVIOUR

In the case of specimens exposed to distilled water the diffusion was Fickian as expected. The moisture absorption programme developed by Springer [1] was hence used to calculate the maximum weight gain and time of saturation analytically. Using these values fractional weight gain  $G$  and dimensionless diffusion parameter  $\ln D_e t/h^2$  were calculated.

The data points were plotted on the analytical curve as shown in Figure 4. Very good correlation exists between the analytical curve and the experimental data points, indicating the applicability of Fickian diffusion model to the composite specimens immersed in water (0% acid concentration).

In the case of 15% sulphuric acid (Figure 5) there is a slight departure between the experimental values and analytical plot. This is presumably due to an increase in concentration of the bi-molecular species at higher acid concentrations.

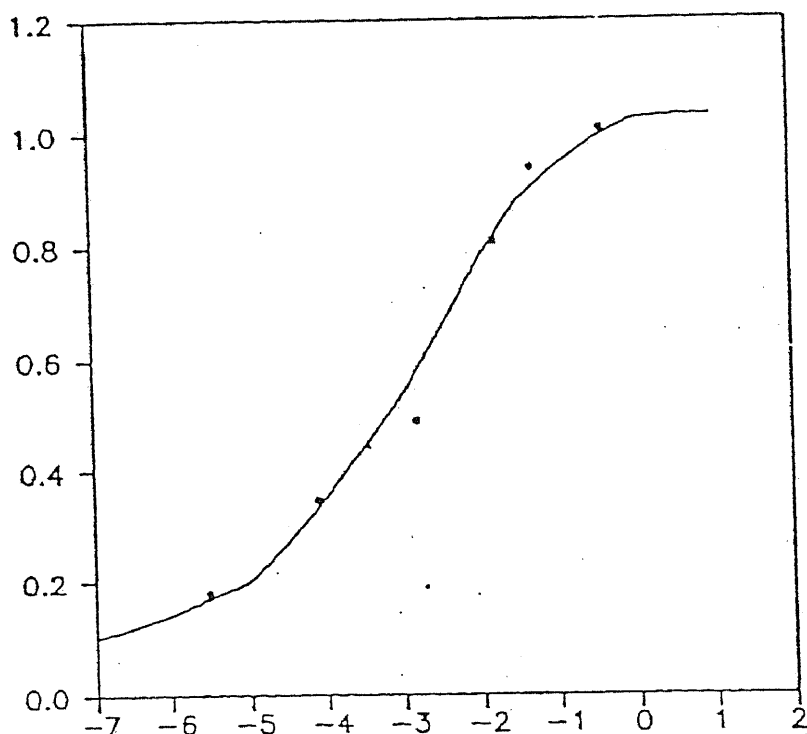


Figure 4. Comparison between analytical and experimental models for composites of isophthalic polyester resin in distilled water. Title: X-axis:  $\text{LN}[D_c/h]$ ; Y-axis:  $G = M/M_m$ .

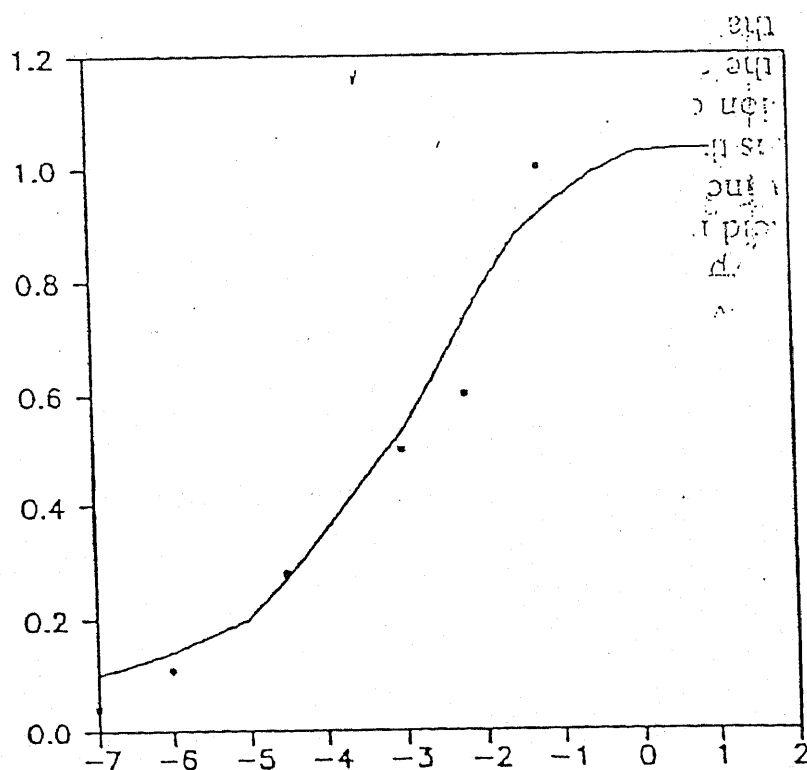


Figure 5. Comparison between analytical and experimental models for composites of isophthalic polyester resin in 15% acid. Title: X-axis:  $\text{LN}[D_c/h]$ ; Y-axis:  $G = M/M_m$ .

Table 1. Diffusion coefficient values for composites of isophthalic polyester resin.

Layup Sequence	Medium	Initial Linear Slope	Max. % Weight Gain	Time of Saturation In Days	Diffusion Coefficient (mm <sup>2</sup> /sec)
A	Distilled water	0.0630	2.38	326.24	0.0006414
A	15% Sulphuric acid	0.0275	2.55	377.87	0.00009518
B	Distilled water	0.0375	1.98	275.73	0.0002817
B	15% Sulphuric acid	0.0245	2.104	486.21	0.0001064
C	Distilled water	0.0280	1.58	159.47	0.0002466
C	15% Sulphuric acid	0.0226	1.98	514.254	0.0001046

The correlations for 15%, 25% and 35% sulphuric acid were unsatisfactory and so they were not used for diffusion analysis. It was decided to use the initial slope of the plot to predict the composite acid absorption behaviour. The slope of the plot at 35% acid is lesser than that at 25% acid indicating that degradation tends to be dominant over diffusion process with increase in acid concentration. An indirect indicator of the onset of degradation is the "kick off" occurring in the per cent weight gain. Comparison of the diffusion coefficient values (for 0%, 15% concentration experiments) indicate that as the acid concentration increases, the diffusion coefficient decreases, indicating that diffusion is tending to become sluggish (Table 1).

### Effect of Fabric Layup Sequence

The layup sequence plays a predominant role in influencing the diffusion process since it determines the available path for the diffusant to enter the specimen. Laminates of CSM and WR type fabrics in isophthalic resin were exposed to acid of 0%, 15%, 25% and 35% concentrations.

Figures 6 to 9 show the percentage weight gain vs the square root of time for these composite specimens.

All composite specimens showed Fickian behaviour in distilled water. Composite specimens of layup sequence A immersed in distilled water (refer Figure 6) have the highest initial linear slope and the highest diffusion coefficient when compared to specimens of layup sequence B and C respectively. This is attributable to the presence of loosely bound chopped strand mat on the top and bottom faces of specimens thus facilitating an easy path for the diffusant. Obviously the presence of more compact woven roving mat on the top and bottom surfaces in the case of layup sequence B and C is the cause for the lower values of initial linear slope and diffusion coefficient in the respective composites.

In the case of composites dipped in 15% acid, the overall diffusion coefficient of composites with layup sequence C is the lowest and that of the composites with layup sequence A is the highest. This signifies that diffusion is more sluggish in the former composites, due to the degradation in these composites and the chang-

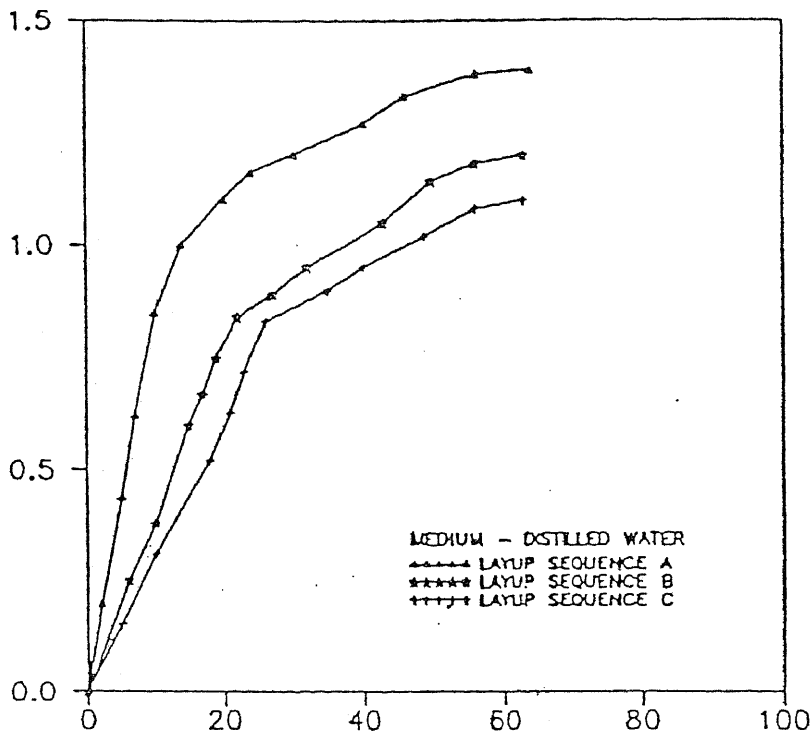


Figure 6. Effect of layup sequence on percentage weight gain values of composites in distilled water. Title: X-axis: root time in  $(hr^{1/2})$ ; Y-axis: percentage weight gain.

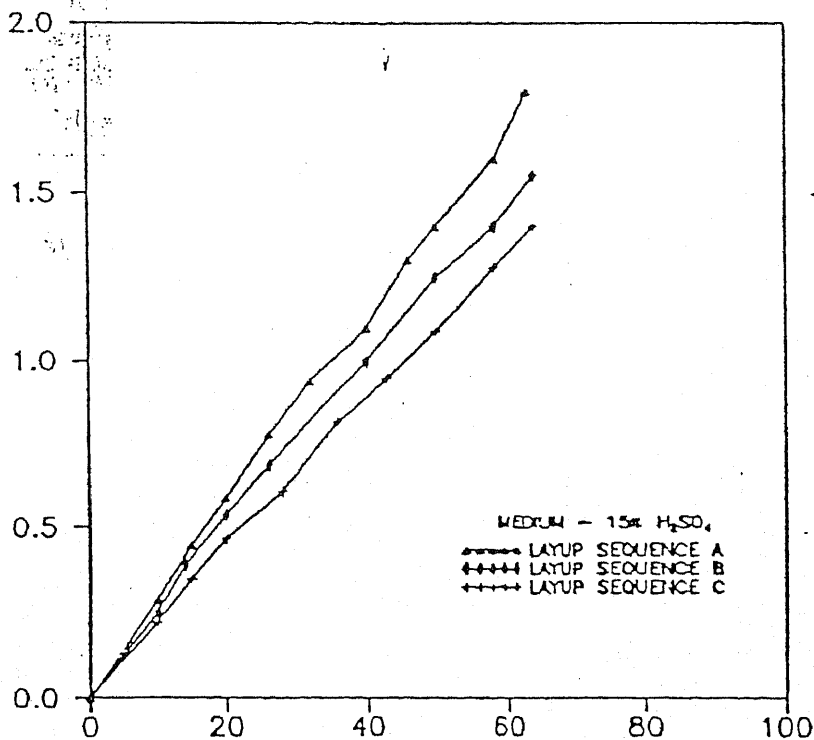


Figure 7. Effect of layup sequence on percentage weight gain values of composites in 15% acid. Title: X-axis: root time in  $(hr^{1/2})$ ; Y-axis: percentage weight gain.



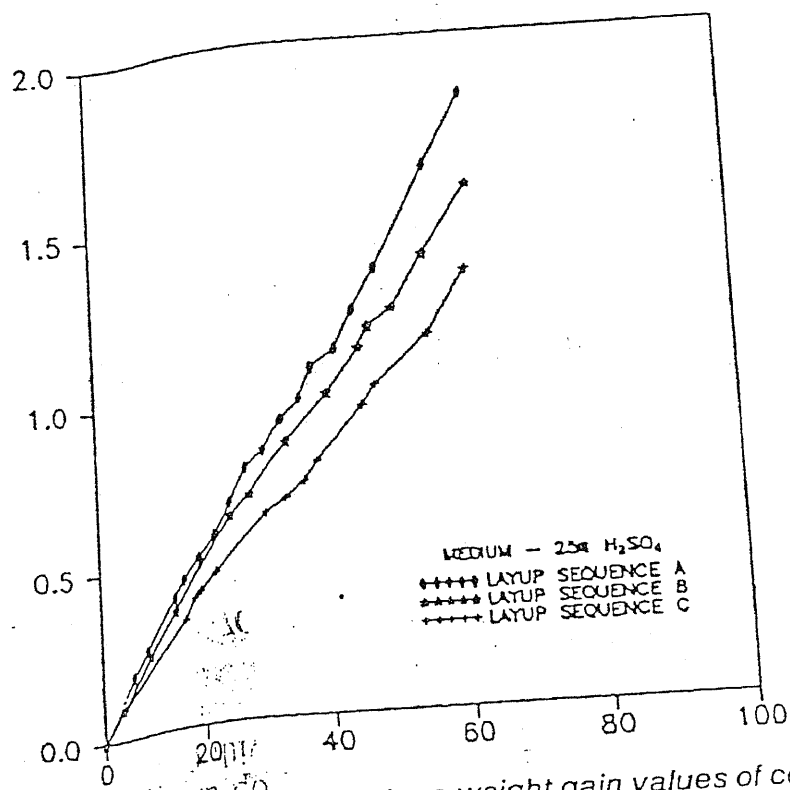


Figure 8. Effect of layup sequence on percentage weight gain values of composites in 25% acid. Title: X-axis: root time in  $(hr)^{1/2}$ ; Y-axis: percentage weight gain.

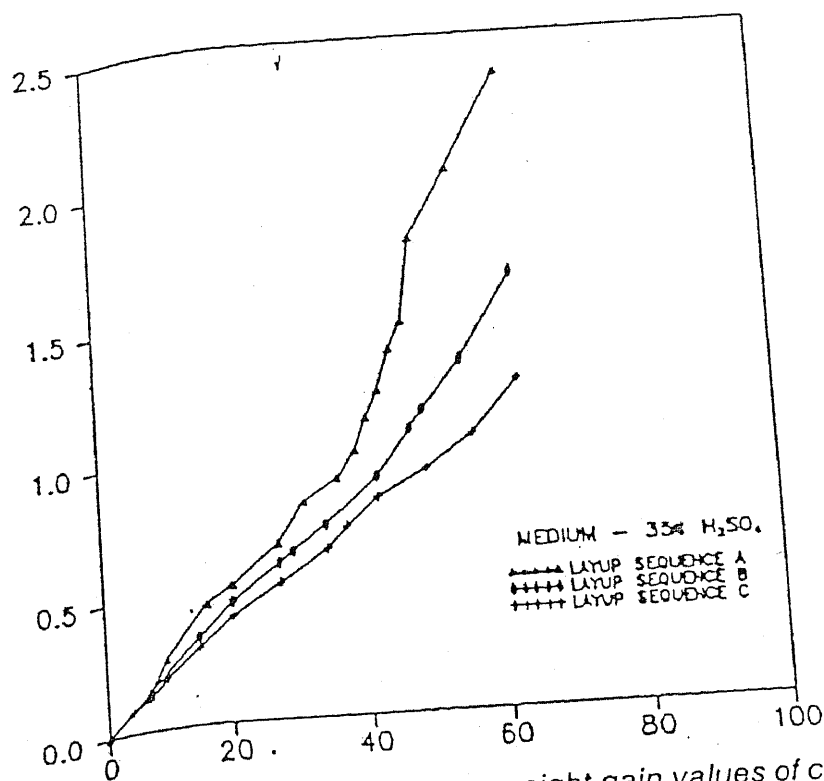


Figure 9. Effect of layup sequence on percentage weight gain values of composites in 35% acid. Title: X-axis: root time in  $(hr)^{1/2}$ ; Y-axis: percentage weight gain.

ing mechanism of absorption. The presence of woven roving in the composite with layup sequence C offers increased stronger barrier to the acid, and hence the fibre matrix interface will tend to be stronger. Thus, in such composites the absorption phenomenon remains fairly diffusion controlled even under acid environments up to certain concentration limits.

The behaviour of composites at higher concentrations was anomalous and hence the performance of the composites had to be judged only by the initial linear slopes of the plots of percentage weight gain vs square root of time. Composites with layup sequence A exhibited the highest initial slope while those with the layup sequence C the least. Once again, the explanation that the presence of a loosely held chopped strand mat on the top and bottom surfaces is the cause for the increase in the percentage weight gain holds good.

### CONCLUSIONS

1. Isophthalic polyester grade resin exhibits superior resistance to sulphuric acid; while general purpose polyester grade resin exhibits least resistance, with epoxies and other polyester grades falling in between.
2. Experimental data for composites of isophthalic polyester resin have good correlation with analytical Fickian diffusion model in the case of immersion in distilled water. This is irrespective of the fabric layup sequence.
3. For all the layup sequences considered, the diffusion process becomes sluggish as the acid concentration increases. At higher concentrations (25% onwards) the diffusion is anomalous. This is attributed to the influence of bi-molecular species on diffusion at higher acid concentration.
4. Among the various fabric layup sequences considered, composites of type C (with woven roving mat on top and bottom) exhibit superior resistance to acid, while those of type A (with CSM on top and bottom) exhibit the least resistance.

### ACKNOWLEDGEMENTS

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